The Impurities in an Acid-Washed 1° Coke-Oven Benzene.
Concentration of Impurities by Progressive Freezing

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A knowledge of the impurities in an acid refined 1° coke-oven benzene was required for the logical selection of methods for the purification of this product. Surprisingly little definitive information is available on the impurities, other than thiophene and carbon disulfide, in refined coke-oven benzene. Stinzendörfer (14)* reported that naphthenes of the methylcyclohexane type prevailed in a residual gasoline fraction obtained in the purification of European coke-oven benzene. Anderson and Engelder (6) prepared a sample of saturated non-benzenoid hydrocarbons from nitration-grade coke-oven benzene by fractional crystallization and fractional adsorption. From the condensation temperatures and refractive indexes of the fractions obtained by efficient distillation of this sample, they inferred the presence of cyclohexane; methylcyclohexane; 3-methylhexane and/or 3-ethylpentane; n-heptane and/or 2,2,4-trimethyl pentane; 1,1-dimethylcyclopentane; and trans-1,2-dimethylcyclopentane and/or trans-1,3-dimethylcyclopentane. A small concentration of toluene was detected, and appreciable concentrations of unsaturated impurities were also indicated. They estimated that the original nitration-grade benzene contained 0.6 volume per cent saturated nonbenzenoid hydrocarbons, 0.004 volume per cent toluene, and 0.1 volume per cent unidentified components.

Anderson, Jones, and Engelder (7) examined the recycle material from the catalytic ethylation of refined coke-oven benzene by the same methods. Any or all of the following paraffins and naphthenes were possible: 2,2-dimethylbutane; 2,3-dimethylbutane; 2-methylpentane; 3-methylpentane; n-hexane; 2,2-dimethylpentane; 2,4-dimethylpentane; 2,2,3-trimethylbutane, 3,3-dimethylpentane; 2,3-dimethylpentane; 2-methylhexane; 3-methylhexane; 3-ethylpentane; n-heptane; 2,2,4-trimethylpentane; cyclopentane; methylcyclopentane; cyclohexane; 1,1-dimethylcyclopentane; trans-1,3-dimethylcyclopentane; trans-1,2-dimethylcyclopentane; cis-1,2-dimethylcyclopentane; cis-1,3-dimethylcyclopentane; and methylcyclohexane. However, the authors observed that some lower-boiling paraffins (2-methylpentane, 3-methylpentane, and n-hexane) appeared to have been introduced during the ethylation process; while most of the naphthenes (except cyclohexane) in the original benzene appeared to have been largely removed. In addition to this serious objection, the inherent limitations of the methods employed in both studies by Anderson and his associates make it virtually impossible, without prohibitive effort, to prove conclusively that any particular compound is present and to measure its concentration accurately.

Kimura and Yasui (11) identified methylcyclohexane and 2,2,4-trimethylpentane in the residue from the commercial chlorination of benzene.

In the present work, the components of virtually the entire impurity content of a conventionally acid-washed 1° coke-oven benzene have been identified positively, and their concentrations have been measured.

* See References

Apparatus

A Perkin-Elmer Model 154-B Fractometer, equipped with a precision temperature controller, was used for the gas-liquid chromatographic separations. Samples were introduced by means of Perkin-Elmer calibrated capillary pipets. The following columns were used:

(1) Two 2-meter by 0.25-inch-diameter stainless-steel-tubing columns of Perkin-Elmer Corporation "A" material (didecyl-phthalate on Celite 545, proportions unknown).

(2) A 25-foot by 0.375-inch-diameter copper-tubing column of polypropylene glycol 2025 (Union Carbide Chemicals Company) on 30-60 mesh Fisher Column Packing in the proportions 31:69.

(3) A 40-foot by 0.375-inch-diameter copper-tubing column of a mixture of o- and p-benzylbiphenyls on 30-60 mesh Burrell Inert Carrier in the proportions 24:76.

The mass spectrometric analyses were performed with a Consolidated Model 21-103C mass spectrometer.

Reagents

All of the pure compounds for calibration of the gas chromatograph and the mass spectrometer were either standard samples from the American Petroleum Institute or research grade materials from the Phillips Petroleum Company.

The benzylbiphenyl was prepared by the procedure of Goldschmiedt (10). The particular sample of benzylbiphenyl that was used as the stationary phase in gas-liquid chromatography was a mixture of predominantly the o- with the p-isomer, with a crystallizing point of approximately 65°.

Procedure

The benzene selected for this study of impurities was a typical, refined, 1° coke-oven benzene, from the high-temperature carbonization of bituminous coal in modern by-product ovens. This benzene was produced by washing crude benzene-toluene-xylene mixture from coal-tar light oil with 66° Baume sulfuric acid in the conventional manner, neutralizing, and distilling. The benzene had a total distillation range (2) of 79.8 - 80.4 C. Its freezing point (3) was 5.07° C, and its purity (4) was 99.30 mole per cent. Its total sulfur content, determined by a combustion procedure, was 177 ppm. Its thiophene content, determined by the isatin method, was 444 ppm. Its carbon disulfide content by the diethylamine-cupric acetate method was 0.36 ppm. Its bromine index by the proposed ASTM potentiometric titration method was 1.8, which corresponds to 0.00088 mole per cent olefin, if it is assumed that, at worst, all the bromine reacted on an equimolar basis with olefins, and that none reacted with the thiophene. This maximum olefin content is so low that this benzene can be considered to be virtually olefin-free.

Preliminary gas-liquid chromatographic examination of the refined 1° benzene showed that the concentrations of some of the impurities were so small that they must be enhanced to permit certain identification. Schwab and Wickers (13) first introduced the method of progressive or slow fractional freezing for the purification of materials, like benzoic acid, that freeze above room temperature. Dickinson and Eaborn (9) adapted the method to the purification of materials, like benzene, that freeze below room temperature. The principle of either version of

the method is the slow advancement of the solid-liquid interface into the liquid phase. This advancement must be so slow that there is ample opportunity for impurities to be rejected by the freezing solid into the remaining liquid. When most of the sample has frozen, the remaining impure liquid can be removed mechanically, and the purification has been effected. This process requires very simple apparatus and very little effort. The time required compares very favorably with that needed for a careful fractional distillation, and quite small samples can be handled. The efficiency of the purification is impressively high, and the principle is asserted to be superior to zone melting involving a single zone.

If this process can be used to purify a material, then, by the same token, it can be used to concentrate the impurities from that material. To test this argument, part of Dickinson and Eaborn's work was repeated as follows: Approximately 20 ml of thiophene-free ACS-specification benzene was placed in a glass-stoppered test tube, 14 millimeters in internal diameter, 140 mm in length below the tubulure, and approximately 22 ml in volume. This tube, suitably counter-weighted, was lowered by a miniature windlass (driven by an electric clock motor, 1 revolution per hour) at a rate of 3 cm per hour into an ice-water bath maintained at constant level. At the beginning of the experiment, the tip of the tube was touched briefly with a small piece of dry ice to start crystallization and avoid supercooling. Approximately 90 per cent of the sample was frozen after 3 hours. The liquid 10 per cent was withdrawn with a hypodermic syringe, the solid was melted, and the process was repeated until six freezings had been performed. The starting material, the six liquid portions withdrawn, and the final purified material were all subjected to gas-liquid chromatographic analysis on the Perkin-Elmer "A" column at 80.5° C. The chromatogram of the liquid withdrawn after the first freezing displayed six impurity peaks, which were 1.13, 1.50, 4.26, 4.50, 2.17, and 6.04 times as large as the corresponding peaks in the chromatogram of the original benzene. For each liquid portion withdrawn after each successive freezing, the impurity peaks became smaller. The purified material left after the sixth freezing was pure benzene by this test; there were no impurity peaks whatever in its chromatogram. Dickinson and Eaborn's preparation of pure benzene was therefore confirmed, and the application of their technique to the preparation of concentrated impurities is valid. Some time after this work was done, Matthews and Coggeshall (12) also demonstrated the application of progressive freezing to the concentration of impurities from organic compounds.

One obvious extension of the progressive-freezing technique is its application in cascade. For this purpose, a large glass-stoppered test tube (27 mm in internal diameter, 380 mm in length below the tubulure, approximately 230 ml in volume) was substituted for the smaller test tube. This tube, suitably counter-weighted, could be lowered into an ice-water bath, maintained at constant level, by the same windlass arrangement at 5 centimeters per hour. Approximately 90 per cent of a 200-ml sample of the refined 1° coke-oven benzene was progressively frozen in this apparatus in 8 hours. The remaining 20 ml of liquid ("10 per cent off, first pass, first freezing") was withdrawn by syringe and subjected to another progressive freezing in the smaller test tube. Again 90 per cent was frozen and the remaining 2 ml of liquid ("10 per cent off, first pass, second freezing" or "concentrated impurities") was withdrawn. The original refined 1° benzene and the 10 per cent portions withdrawn in the first and second freezings were chromatographed on the polypropylene glycol 2025 column at 121° C. The resulting chromatograms, Figure 1, show the increases in concentrations of impurities that are achieved by cascade operation. In this figure, the three chromatograms have been displaced vertically from each other to a slight extent for the sake of clarity. The en-circled numbers designate the various peaks. The attenuation factors are marked near the peaks. In Table I, the heights of the easily measurable impurity peaks in these three chromatograms are tabulated. The first freezing produced a two- to threefold increase in most of the peaks; the second freezing produced a nearly

twofold increase over the first. Cascade operation therefore produced approximately a fivefold increase in most of the peaks. The cascade method was therefore adopted for the production of "concentrated impurities" from the refined 1° benzene.

In view of the extremely small concentrations of some of the impurities in the refined 1° benzene, all the qualitative analyses were performed on the concentrated impurities. The benzylbiphenyl column, originally described by Desty and Whyman (8), was used for all the gas-liquid chromatographic separations, because of its superior resolving power for aromatics and paraffins. This column was operated at 121° C, and 500 μl (nominal) of sample was introduced. A typical chromatogram is shown in Figure 2. The very large sample volume was used to supply detectable amounts of the minor impurities, such as those in peaks 1 and 6. To obtain additional information to supplement the chromatographic data, so that qualitative identifications could be made with certainty, each peak in the chromatogram was collected in a trap cooled in liquid nitrogen. The contents of each trap were then analyzed by mass spectrometry. In each case, the mass spectrum of the contents of the trap was first corrected for the very small contribution of the "column blank"--the very small amount of the stationary phase and/or its decomposition products that is vaporized constantly from the chromatographic column and is caught in the trap when it is cooled. The hydrocarbon-type analysis developed originally by Brown (5) was next applied to each mass spectrum to facilitate its interpretation. When the relative retention volume for a chromatographic peak was used to narrow the choice of possible components contributing to that peak, it was then usually rather simple to confirm or reject each of the possible components from the mass spectrum. The relative retention volumes of a small number of pure hydrocarbons were determined under the conditions prevailing in the qualitative analysis, that is, on the benzylbiphenyl column at 121° C, "flooded" with 500 μl of benzene. From these data and the published values for a large number of compounds at 78.5° C (8), the relative retention volumes at 121° C for these compounds could be estimated with sufficient accuracy for the preliminary qualitative analyses. Once the presence of a compound had been established by the preliminary chromatographic and mass-spectrometric data, its presence was further confirmed by direct experimental measurement of its relative retention volume on the benzylbiphenyl column at 121° C, "flooded" with 500 μl of benzene. Similarly, published mass spectra (1) were used for the preliminary interpretations, but once the presence of a compound had been thus established, its mass spectrum was determined by direct experimental measurement with the Model 21-103C spectrometer. The qualitative compositions of the substances producing the peaks in the chromatogram in Figure 2 are shown in Table II. As more than one compound contributed to each impurity peak and as progressive freezing affected the concentrations of the compounds contributing to any peak to different unknown extents, it was obviously necessary to perform the quantitative analysis directly on the original 1° benzene.

The quantitative analyses were performed by collecting quantitatively in a cold trap the substance producing each peak in the gas chromatogram of a known amount of the original 1° benzene (similar to Figure 2, but with smaller impurities peaks). The time intervals marked above the chromatogram in Figure 2 are identical with those used in the trappings for the quantitative analyses. The entire contents of the trap were then admitted to the mass spectrometer and analyzed quantitatively. Since the concentrations of the several impurities varied over a very wide range, not all of the peaks could be trapped from a single sample of the 1° coke-oven benzene. The amount of sample used in each case is shown in Table II. For a very minor impurity, 500 μl (nominal), which is the practical maximum accommodated by the chromatographic column, would provide too small an amount of impurity for spectrometric analysis. In that case, a sufficient number of 500-μl (nominal) portions of the 1° benzene was chromatographed in succession to supply the necessary amount of impurity for the spectrometric analysis. When the desired chromatographic peak appeared in each chromatogram,

the same collecting trap was applied to the vent line of the chromatograph until the necessary total amount of that impurity had been collected.

Because this whole procedure can be no more accurate and precise than the quantitative operation of the cold traps, these were studied carefully. The first traps used were simple U-shaped lengths of capillary tubing 2 mm in internal diameter and 18 inches in length, provided with vacuum stopcocks near each end and a standard taper joint at one end (8). Six such traps were used with a manifold arrangement connected to the vent line of the chromatograph. The possibility of absorption of minor components by stopcock grease and occasional plugging of the capillary by frozen condensate led to the adoption of a simpler system, which was used for all the final quantitative analyses. A short glass Y-tube was butted against the end of the vent line of the chromatograph. The butt joint was held in place with Tygon tubing. The traps were of the conventional concentric tube design, 175 mm long, with the inner tube 6 mm in external diameter and the outer tube 16 mm in external diameter. The inner tube ended 15 mm above the bottom of the outer tube. One of these traps was connected to each arm of the Y-tube with a section of Tygon tubing just long enough to permit the application of a hosecock clamp. A drying tube filled with Ascarite was connected with a similar short length of Tygon tubing and clamp to the exit tube of each trap to minimize back-diffusion of moisture and carbon dioxide into the trap when it was chilled. Each trap was purged at room temperature with helium before use. As there were no stopcocks in the system, grease was eliminated. By connecting the traps to the Y-tube and manipulating the clamps at the proper times, any peak could be collected in a trap. Although this arrangement was not quite as fast or convenient as the manifold with stopcocks, it did eliminate the possibility of partial loss of components by absorption in stopcock grease. The traps were immersed to only about one-half to two-thirds of their length during use. As soon as the trapping was completed, the liquid nitrogen level was raised so that the entire length was immersed. By this procedure, loss of trapped material by warming of condensate in the upper part of the trap should be eliminated. The trap was butted to the mass-spectrometer inlet system with Tygon tubing, and its entire contents were analyzed quantitatively in the usual way.

The performance of this entire procedure was tested by introducing known amounts of pure compounds or known mixtures into the gas chromatograph, collecting the components in the chilled traps connected to the chromatograph vent line, and measuring the amounts collected by mass spectrometry. Pure n-heptane was used first. In seven tests, the recovery achieved was 80, 94, 114, 106, 109, 108, and 101 per cent of the amount introduced. A mixture comprising 62.7 volume per cent n-heptane and 37.3 volume per cent cyclohexane (mass spectrometric analysis) was tested next. Each component was trapped individually. In duplicate tests, 108 and 108 per cent of the heptane and 101 and 101 per cent of the cyclohexane introduced were recovered. From these data, the apparent recovery achieved with the procedure might be estimated at 100 ± 10 per cent, although, for reasons unknown, recoveries outside these limits, particularly on the low side, may be observed occasionally.

Positive errors (recoveries higher than 100 per cent) may be caused by 1) excess liquid sample clinging to the outer surfaces of the capillary pipette with which samples are introduced into the gas-liquid chromatograph, and/or 2) error in the calibration of the very small capillary pipette (0.5 µl) with which pure liquids are introduced into the mass spectrometer for calibration. The first error is variable; the second is constant. The first error was minimized by touching only the very tip of the pipette to the surface of the liquid sample, removing the pipette from contact with the liquid, and waiting perhaps 15 seconds before introducing the sample into the chromatograph. By this procedure, the excess liquid is minimized at the outset, and the very small excess that cannot

be avoided has time to evaporate. The second error is caused by the difficulties during calibration of filling with mercury the very tiny volume of the mass spectrometer pipette and emptying it completely. Beyond exercising the utmost care in all the manipulations and replicating the calibration with good repeatability, the authors know of no obvious improvement.

Negative errors (recoveries lower than 100 per cent) may be caused by 1) failure to introduce the entire sample into the chromatograph, 2) less than quantitative trapping, and 3) losses in introducing the trapped sample into the mass spectrometer. Gross errors of the first kind can be detected immediately by variations in the peak heights in the chromatogram, and the test can be rejected. The second error is difficult to isolate and study. Packing the trap or increasing the contact of the vapor with the trap walls in other ways might increase the efficiency of trapping, but might also make it more difficult to vaporize all the condensate into the mass spectrometer or to clean the trap for reuse. The third error was minimized by eliminating stopcock grease from the spectrometer inlet system by butting the trap to it with Tygon tubing.

Two special modifications of the standard concentric cylindrical traps were made. When peak No. 9 (Figure 2), the small peak on the long tail of the very large peak No. 8, was trapped, sizable amounts of the material of peak No. 8 were collected and plugged the ordinary trap. A special trap was therefore made to avoid this difficulty, with the external tube 24 mm in outside diameter and 115 mm long, and the internal tube 15 mm in outside diameter and 100 mm long. This trap was amply large to accommodate all the material collected. When peak No. 8 was collected, this trap was still large enough, but in this case it was desirable to introduce the collected material into the mass spectrometer as a liquid. For this reason, a small tip, 8 mm in diameter and 35 mm long, was blown into the bottom of one of the special traps. After the material from peak No. 8 had been collected in this trap, the frozen condensate was melted into the small tip, which was then broken off to make the liquid available.

All the quantitative analyses were performed in duplicate at least. In view of the fact that those errors (described above) that are most difficult to control all tend to cause less than quantitative recoveries, replicate analyses that gave low results were regarded with suspicion and repeated.

Results and Discussion

The qualitative and quantitative analyses of the mixtures producing each of the ten peaks in the chromatogram of the 1° coke-oven benzene on the 40-foot benzylbiphenyl column at 121° C are tabulated in Table II. In every case, the residual mass spectrum remaining after the contributions of these components had been calculated was examined. For peaks No. 1, 2, 3, 4, 5, 8, 9 and 10, these residuals were within the expected mass spectrometric error, that is, no residual peak was larger than 3 per cent of the largest peak in the mass spectrum and was usually appreciably less. For these mixtures, it is highly probable that no additional components (beyond those listed in Table II) would be identified at concentrations exceeding approximately 0.005 mole per cent (in each mixture) in any more exhaustive investigation. For peak No. 7, the largest residual mass peak was 4.3 per cent of the height of the largest peak in the spectrum. Moreover, residual peaks occurred at masses 43, 57, 69, 71, 85 and 97, which were 3 to 4 per cent of the height of the largest peak. It is highly probable that some unidentified alkanes and/or naphthenes, present at a total concentration of less than approximately 0.03 mole per cent, account for these peaks. This is approximately 4 per cent of the total 0.70 mole per cent impurity determined cryoscopically.

The type analysis calculated from the mass spectrum of peak No. 6 showed 86 per cent naphthenes and 13 per cent alkanes, with an average carbon number of 8. From the mass spectrum, the naphthene is very probably a trimethylcyclopentane. The specific isomer could not be identified, however, because only six of the possible eight geometric isomers of trimethylcyclopentane (excluding stereoisomers) have been prepared in the pure state and their mass spectra published. The relative retention volume of peak No. 6 also confirms the hypothesis that the naphthene is a trimethylcyclopentane. The impossibility of identifying the naphthene specifically also makes it impossible to identify the accompanying alkane specifically. From the mass spectrum and the relative retention volume, the alkane is very probably an octane. The estimates of the concentrations of the naphthene and the alkane were made from average published values for the mass spectrometric sensitivities for trimethylcyclopentanes and octanes, respectively. These are only estimates, but peak No. 6 in any case accounts for only about 1.5 per cent of the total impurities.

Appreciable concentrations of impurities might be obscured by the very extensive benzene peak (similar to peak No. 8, Figure 2). The material producing this peak was therefore collected and analyzed as previously described. This material was benzene of even higher purity than the benzene of 99.93 mole per cent purity that was used for calibration. The probability of any appreciable concentration of impurities being obscured by the benzene peak is therefore slight.

The chromatograms of "concentrated impurities" on the polypropylene glycol 2025 (Figure 1) and the benzylbiphenyl (Figure 2) columns exhibited three and one peaks, respectively, arriving before peak No. 1. As the total concentrations of the component(s) producing these peaks are very probably appreciably less than one part per million, no attempt was made to collect and identify them.

It can be seen from Table II that most of the 2-methylhexane was found in peak No. 2, but that a small amount was also found in peak No. 3. This is a direct consequence of the fact that the 2-methylhexane had not been completely eluted with the other components of the first peak, before the components of the second peak of the pair began to elute. Similarly, most of the n-heptane was found in peak No. 4, but a small amount was found in peak No. 5. However, as long as both peaks of each pair are trapped from the same sample introduction, no error is caused by this partial failure to resolve the components. This procedure was followed in each of these cases.

In Table III, therefore, the qualitative and quantitative analyses of the impurities have been tabulated on a cumulative basis, without regard to the distribution of a component between two peaks. The concentrations are expressed as volume, weight, and mole per cent, all based on the whole benzene sample. A total of 20 impurities was identified -- 8 alkanes, 8 naphthenes, 1 aromatic, and 1 heterocyclic compound with certainty; and 1 alkane and 1 naphthene with good probability. Neither olefins nor carbon disulfide were detected, as was expected from their very low concentrations. The 501 ppm thiophene determined here agrees fairly well with the 444 ppm found by the isatin method. The average 4.4 per cent of the impurities unaccounted for agrees well with the approximately 4 per cent unaccounted for in peak No. 7.

For all the specifically identified components present in concentrations exceeding 0.007 mole per cent (1 per cent of the total impurity), the average repeatability of the determinations was ± 3.9 per cent; the worst repeatability was ± 9.9 per cent. For all the specifically identified components present in concentrations less than 0.007 mole per cent, the average repeatability was ± 8.3 per cent; the worst repeatability was ± 24.2 per cent. Over-all repeatability, calculated from the total impurities found, was ± 2.7 per cent. The accuracies

of individual analyses cannot be estimated; in fact, the only indication of accuracy is the total average recovery, 95.6 per cent of the total impurity measured by the cryoscopic method, which is usually highly accurate for a sample of this kind.

The occurrence in coke-oven benzene of 2,2-dimethylpentane; 2,4-dimethylpentane; 2-methylhexane; 3,3-dimethylpentane; 2,3-dimethylpentane; 3-methylhexane; 3-ethylpentane; 1,trans-2 dimethylcyclopentane; 1,trans-3 dimethylcyclopentane; and 1,cis-2 dimethylcyclopentane, which had been identified tentatively by Anderson and his associates (6, 7), has now been established definitely. 1,trans-2, cis-4 trimethylcyclopentane has been identified in coke-oven benzene for the first time. (The occurrence of another trimethylcyclopentane is highly probable.) Eleven new products of the high-temperature carbonization of bituminous coal have therefore been established with certainty.

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Table I

Enhancement of Concentrations of Impurities in 1° Coke-Oven Benzene
by Cascade Application of Progressive Freezing

Peak Number (Figure 1)	Chromatogram Peak Height, arbitrary units		
	Original 1° Benzene	"10% Off, First Pass, First Freezing"	"10% Off, First Pass, Second Freezing" "Concentrated Impurities"
1	0.2	0.7	1.7
2	9.6	25.7	53.6
3	13.4	35.4	74.2
4	47.4	124	251
5	20.2	53	99
6	--	--	3.7
7	2	8	19
9	--	4.3	6.0
10	0.4	1.0	2.8

Table II

Qualitative and Quantitative Analyses of the Individual Peaks in the
Gas-Liquid Chromatogram of 1° Coke-Oven Benzene

Peak No. (Figure 2)	Total Volume of Sample, μl	Component	Analysis, Mole % Based on Benzene Sample		
			Trial 1	Trial 2	Average
1	1514.4	2,2-dimethylpentane	0.000130	0.000116	0.000123
		2,4-dimethylpentane	0.000747	0.000454	0.000601
2	1009.6	2-methylhexane	0.0231	0.0221	0.0226
		3,3-dimethylpentane	0.000870	0.000827	0.000849
		methylcyclopentane	0.00597	0.00599	0.00598
3	1009.6	2-methylhexane	0.000308	0.000425	0.000367
		methylcyclopentane	0.000671	0.000648	0.000659
		2,3-dimethylpentane	0.0156	0.0134	0.0145
		3-methylhexane	0.0251	0.0232	0.0242
4	169.4	n-heptane	0.0880	0.0844	0.0862
		1,1-dimethylcyclopentane	0.00697	0.00682	0.00690
		3-ethylpentane	0.00523	0.00406	0.00465
5	169.4	n-heptane	0.00490	0.00529	0.00510
		cyclohexane	0.0644	0.0613	0.0629
		1,trans-2 dimethylcyclopentane	0.0550	0.0447	0.0499
		1,trans-3 dimethylcyclopentane	0.0448	0.0487	0.0468
6	1514.4	a trimethylcyclopentane (?)	~ 0.00690	~ 0.00950	~ 0.00820
		an octane (?)	~ 0.0010	~ 0.0010	~ 0.0010
7	169.4	methylcyclohexane	0.229	0.214	0.222
		1,cis-2 dimethylcyclopentane	0.0196	0.0181	0.0189
		1,trans-2,cis-4 trimethylcyclopentane	0.00744	0.00677	0.00711
8	169.4	benzene	Pure benzene		
9	169.4	benzene		0.4777	
		thiophene	0.0466	0.0465	0.0466
10	1009.6	benzene	0.0862	0.0959	0.0911
		toluene	0.0330	0.0338	0.0334

Table III

Qualitative and Quantitative Analyses of the Impurities in 1° Coke-Oven Benzene

| Peak No. (Figure 2)	Normal Boiling Point of Pure Component, °C	Component	Mole Per Cent Trial 1	Mole Per Cent Trial 2	Average Mole %	Average Vol %	Average Wt %
1	79.205	2,2-dimethylpentane	0.000130	0.000116	0.00012	0.00021	0.00016
	80.51	2,4-dimethylpentane	0.000747	0.000454	0.00060	0.0010	0.00077
	90.05	2-methylhexane	0.0234	0.0225	0.0230	0.0381	0.0295
2 & 3	86.071	3,3-dimethylpentane	0.000870	0.000827	0.00085	0.0014	0.0011
	71.812	methylcyclopentane	0.00664	0.00648	0.00656	0.0083	0.0071
	89.79	2,3-dimethylpentane	0.0156	0.0134	0.0145	0.0235	0.0186
	91.95	3-methylhexane	0.0251	0.0232	0.024	0.039	0.031
	98.428	n-heptane	0.0929	0.0897	0.0913	0.150	0.117
	87.84	1,1-dimethylcyclopentane	0.00697	0.00682	0.0069	0.010	0.0087
4 & 5	93.468	3-ethylpentane	0.00523	0.00406	0.0047	0.0075	0.0060
	80.738	cyclohexane	0.0644	0.0613	0.063	0.077	0.068
	91.87	1,trans-2 dimethyl cyclopentane	0.0550	0.0447	0.050	0.063	0.054
	90.77	1,trans-3 dimethyl cyclopentane	0.0448	0.0487	0.047	0.060	0.051
6		a trimethylcyclopentane (?)	~0.0069	~0.0095	~0.0082	~0.014	~0.012
		an octane (?)	~0.0010	~0.0010	~0.0010	~0.0018	~0.0015
	100.934	methylcyclohexane	0.229	0.214	0.222	0.319	0.279
7	99.53	1,cis-2 dimethyl cyclopentane	0.0196	0.0181	0.019	0.027	0.024
	109.28	1,trans-2,cis-4 trimethylcyclopentane	0.00744	0.00677	0.0071	0.012	0.010
9	84.1	thiophene	0.0466	0.0465	0.0466	0.0411	0.0501
10	110.623	toluene	0.0330	0.0338	0.0334	0.0396	0.0392
Total			0.685	0.652	0.670	0.933	0.808
% of the total 0.70 mole % impurity accounted for			97.9	93.1	95.6		
% of the total 0.70 mole % impurity unaccounted for			2.1	6.9	4.4		
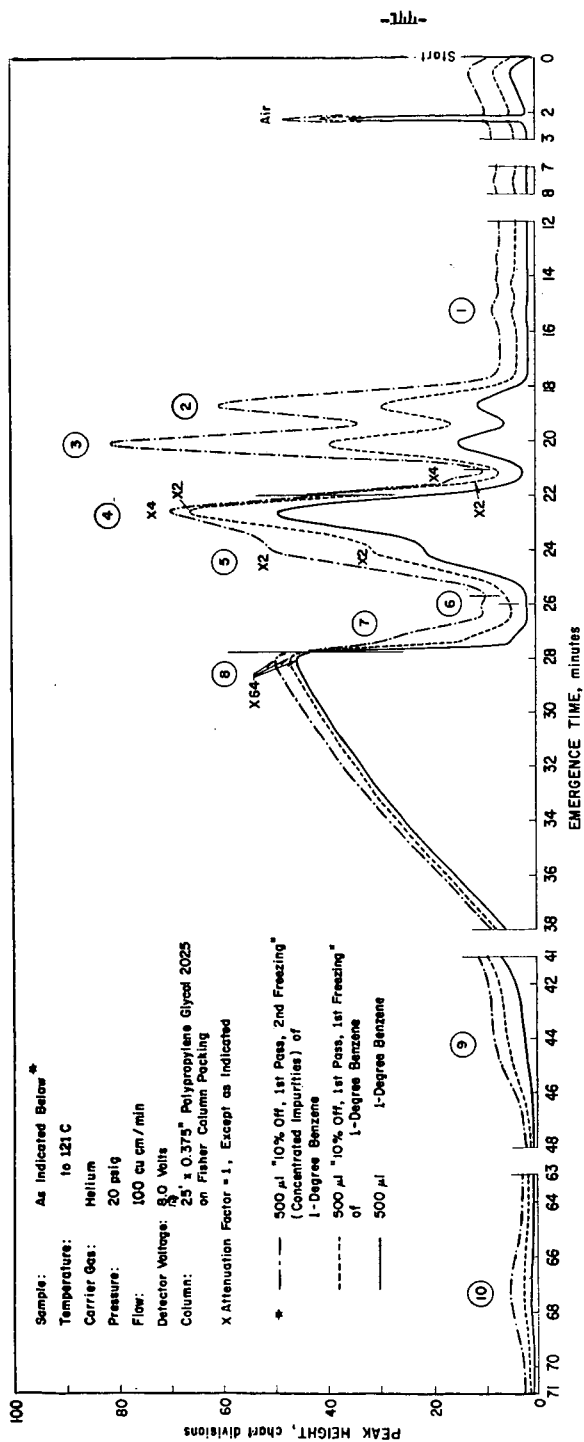
Figure 1. Gas-liquid Chromatograms Showing Enhancement of Concentration of Impurities in 1-Degree Benzene

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Figure 2. Gas-Liquid Chromatogram of Concentrated Impurities From 1-Degree Benzene